A Rhenium Polyphenyl Complex: *X*-Ray Diffraction Analysis of Tris(η^1-phenyl)bis(diethylphenylphosphine)rhenium

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Summary An *X*-ray study of the polyphenyl complex $[\mathrm{Re}(\eta^1\text{-Ph})_3(\mathrm{PEt_2Ph})_2]$ reveals a trigonal bipyramidal structure with a near-planar array of equatorial phenyl ligands and relatively short Re–C bond lengths, indicative of significant π-bonding.

TRANSITION metal polyphenyl complexes are, in general, difficult to prepare and relatively unstable. Conceivable decomposition pathways are *via* reductive elimination of biphenyl, or β-hydrogen elimination with formation of benzyne and metal hydride. A classic case is that of Hein's polyphenyl chromium compounds[1] where metal reduction occurs readily, with formation of $\mathrm{Cr^0}$- and $\mathrm{Cr^I}$-η^6-arene complexes. However, the relationship of structure to reactivity in polyphenyl complexes is still poorly understood. We recently became interested in the synthesis and structural characterization of transition metal polyphenyl compounds, particularly those stabilized by phosphine ligands. This report concerns the structural analysis of the diamagnetic 14-electron complex $[\mathrm{Re}(\eta^1\text{-Ph})_3(\mathrm{PEt_2Ph})_2]$ (I), originally reported by Chatt and his co-workers,[2] and represents one of the few accurate studies of such a compound. The structure of a somewhat related anionic polyphenyl compound, $\mathrm{Na_2Cr}(\eta^1\text{-Ph})_5\cdot3(\mathrm{Et_2O})\cdot\mathrm{THF}$ (II) (THF = tetrahydrofuran) has been reported but the accuracy of that structure determination is somewhat low (R = 0·172), and the geometry of the anion is severely distorted due to interactions with the sodium counterions.[3]

Crystal data: crystals of (I), from hexane, are deep blue, monoclinic, space group $C2/c$, a = 15·134(6), b = 13·825(5), c = 18·447(6) Å, β = 118·01(2)°, U = 3407·5 Å^3, D_m = 1·45, D_c = 1·46 g cm^{-3}, Z = 4.

A total of 2137 unique reflections for 10° < 2θ < 45° were collected on a Nonius CAD-3 automated diffractometer using Mo-K_α radiation. The structure was solved by heavy atom methods and all non-hydrogen atoms have been refined isotropically by full-matrix least-squares to a current R of 0·041 for 1887 observed reflections [$I > 3\sigma(I)$]. The gross structure consists of a trigonal bipyramidal arrangement of three equatorial phenyl groups and two axial phosphine ligands about the central rhenium atom (Figure). Looking along the main P–Re–P axis of the

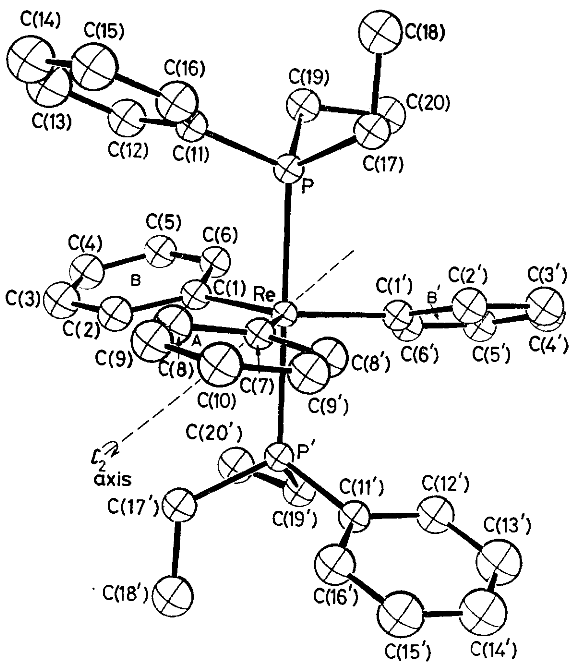

FIGURE. The structure of $\mathrm{RePh_3(PEt_2Ph)_2}$(I), showing the roughly co-planar arrangement of the equatorial phenyl groups. Important distances and angles in the molecule are: Re–P, 2·392(3); Re–C(1), 2·029(10); and Re–C(7), 2·024(11) Å; ∠P–Re–P′, 177·4(1); ∠P–Re–C(1), 92·6(3); ∠P–Re–C(7), 88·7(1); ∠C(1)–Re–C(7), 120·6(2); and ∠C(1)–Re–C(1′), 118·8(2)°.

molecule, one sees that the phenyl rings of the equatorial $RePh_3$ fragment are staggered with respect to the substituents on the phosphorus atoms. The molecule has a crystallographically-imposed C_2 axis, defined by Re, C(7), and C(10). The unique Re–C distances are 2·029(10) and 2·024(11) Å.†

A novel feature of this structure determination is the approximately planar array of equatorial phenyl ligands. The angle between the ring planes A and B is 21·1°, while that between planes B and B′ is 32·5°.The twist angles between the equatorial Re, C(1), C(1′), C(7) plane and planes A and B are, respectively, 4·5 and 18·6°. Complete co-planarity of the rings is restricted by close approach of the *ortho* hydrogen atoms of adjacent rings. Calculated distances between *ortho* hydrogen atoms (assuming C–H = 1·08 Å) are 2·07 Å for rings A and B and 2·16 Å for rings B and B′. In an idealized totally planar arrangement, *ortho* hydrogen contacts would be an intolerable 1·63 Å. It is interesting to compare the structure of the $RePh_3$ group with that of the Ph_3C^+ ion in which a propeller type arrangement is also observed[4] but due to the smaller size of the central atom (C *vs.* Re), adjacent rings are mutually twisted at an angle of 54° to relieve steric interactions between the *ortho* hydrogens. A similar equatorial arrangement of phenyl groups is probably present in (II), but their relative orientations were not clearly specified.[3]

The present study indicates significant metal $d\pi$ to phenyl $p\pi^*$ back donation in that the Re–C bonds [average 2·027(3) Å] are somewhat shorter than expected for a bond of unit order.[5] Thus, assuming that the Re–Me bonds[6] (2·24 Å) in $[Re(\eta^1\text{-}Me)_2(\eta^4\text{-}exo\text{-}C_5H_5Me)(\eta^5\text{-}C_5H_5)]$ are of unit order, and allowing for the 0·02 Å difference in covalent radii between sp^2 and sp^3 carbon atoms,[7] one can estimate a length of 2·22 Å for a Re–C(sp^2) single bond. The contraction observed is well outside experimental error and provides strong evidence for a substantial π-component in the rhenium–phenyl linkage. Again, comparison can be made with the Ph_3C^+ ion where a π-interaction was inferred from shortened C–C bonds between the phenyl groups and the central carbon atom.[4]

Hoffmann has commented[8] on π-bonding effects in trigonal bipyramidal transition metal complexes and re-emphasized the established generalization that strong π-acceptor ligands will tend to occupy equatorial sites. In addition, calculations[9] on the model system $[Re(\eta^1\text{-}Ph)_3(PH_3)_2]$ indicate that a low energy situation arises when the phenyl groups are in the equatorial plane. However, strict coplanarity is obviated by steric interactions and the orientation adopted is obviously a compromise one which still allows substantial π-bonding (as evidenced by the short Re–C bonds) and relieves the steric strain. It has been shown[8,9] that the order $(d_{z^2}) > (d_{x^2-y^2},d_{xy}) > (d_{xy},d_{yz})$ persists for the orbital energies of five-co-ordinate transition metal complexes, and so for the present Re^{III} complex (d^4) one can envisage the predominant mode of backbonding to take place from the filled (d_{xz},d_{yz}) metal orbitals to the empty phenyl π^* orbitals.

It has further been pointed out[8,9] that d^4 low-spin five-co-ordinate complexes represent one of the few cases in which one might expect a large barrier to the interconversion of trigonal bipyramids. Thus, it is interesting to speculate whether other isomers of this compound (*i.e.*, with the phosphines axial–equatorial or equatorial–equatorial) can be isolated.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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